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Overcoming Distrust in Solid State Simulations: Adding Error Bars to Computational Data

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Abstract

Simulations are progressively becoming an everyday tool for the understanding of materials. DFT is without any doubt the working horse in the vast majority of cases in which quantum mechanical effects need to be included for a correct description of the chemical problem. However, unlike other quantum-mechanical methods, DFT approaches cannot be improved in a systematic manner. This leads to distrust and the feeling that calculation parameters can be tuned with the explicit aim of matching the experimental results, even at the expense of the quality of the simulation. More specifically, it would appear that changing the functional can provide any desired quantity to match the experiment. Hereby, we focus on the nature of systematic simulation errors as compared to reproducibility-experimental ones. We show that DFT errors need to be estimated from bracketing physical descriptions. Highlighting the role of the main error affecting DFT calculations, the delocalization error, we show that HF and LDA provide bracketing limits and we develop a simple and robust procedure to quickly provide error bars that help understanding the inherent error of a given calculation. Moreover, for challenging experimental quantities, the experimental and computational error bars become of the same order of magnitude. Overall, this approach should help overcoming distrust in solid state simulations through a detour to the overwhelming question: “which functional to choose?”.

Introduction

A close collaboration between simulation and experiment has become routine in the mutual validation of data. One of the main reasons behind this collaboration is the fact that with the increase in computing power, larger and more complex systems can be calculated at the quantum mechanical level. What often hinders this joint effort is the lack of a degree of uncertainty associated with simulated data, which are usually presented as naked numbers without an associated precision, contrarily to experimental values which are generally accompanied by a range that estimates the precision of the measurement. This often leads,

in the comparison of experimental and calculated results, to shady situations in which objectiveness succumbs to personal interpretation (and wishful thinking): is it acceptable to assert a good agreement between theory and experiment when the calculated value falls just narrowly out of the experimental error range? The temptation to tamper with simulation parameters to have the calculated value nicely falling within the experimental range is hard to resist and gives rise to suspicion in the interaction between computational and experimental chemists.^{1,2} Additionally, in light of the incipient fourth industrial revolution of artificial intelligence, the increasing demand of scientific data is accompanied by a growing concern on their reproducibility and error,³ which is a sore spot for calculated data, chronically lacking an uncertainty estimation. In this work, we aim at changing the paradigm of the experiment-computational interaction, presenting in a clear way how much of the uncertainty on selected properties depends on the method employed in the calculations.

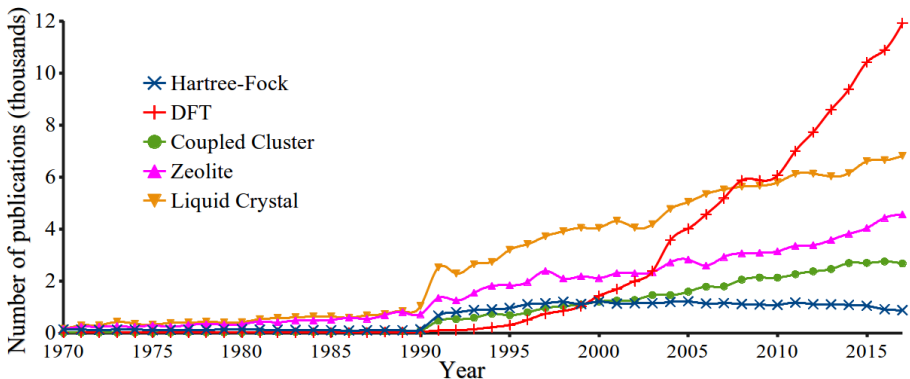


Figure 1: Number of publications (in thousands) per year containing the keywords Hartree-Fock (in blue), DFT (in red), Coupled Cluster (in green), Zeolite (in magenta) and Liquid Crystal (in orange). Results extracted from the ISI Web of Science as of May 2018.

Due to its favorable scaling, DFT is the method of choice in the vast majority of these cases. Figure 1 illustrates the huge preponderance over other methods (more accurate or similar in cost) in terms of number of publications. Some hot topic materials have also been included for reference (e.g. zeolites and liquid crystals), showing that the trend in DFT follows an exponential increase. In this framework, the "random" results imposed by the functional are not an acceptable scientific frame.

Results and discussion

To introduce the problem, we will start with one of the simplest features of a crystal: its cell parameters. Nowadays, a routine X-ray diffractometer measurement provides the cell parameters with an excellent precision, the uncertainty being as low as some parts in 10^{-4} , even for organic crystals, which can be lessened by a further order of magnitude by employing special techniques.⁴ The case of NaCl is emblematic. In the first work by Bragg, dating back to 1913, the value of the cell parameter a_{expt} was set to 4.45 Å, only to be corrected in the same year to the value of 5.62 Å, which is extremely close to the currently accepted value of 5.6401 Å.^{5,6} Owing to its simplicity, the geometry of the unit cell is often one of the first quantities that are checked in the comparison between computation and experiment. In this situation, what is the result of the comparison between $a_{expt} = 5.6401$ Å and an hypothetical calculated value $a_{calc} = 5.7835$ Å with no error bar? With such a difference between a_{calc} and a_{expt} , can we trust the computational technique employed to acceptably represent the real crystal, and therefore draw conclusions based on the physical insight provided by the simulation?

To answer this question we have to investigate the sources of error that affect the value of the calculated cell parameter. A first consideration is that the geometry optimization of a solid, which yields the cell parameters, does not have an associated random error except the numerical one associated to arithmetic operations, which is negligible. This means that irrespective of the number of repetitions, a geometry optimization with the same starting point, method and simulation parameters will always converge to the same structure, and thus to the same a_{calc} value. As a consequence, all the errors in this kind of calculation are systematic and therefore hard to eliminate. The main sources of systematic error are the level of theory employed (the combination of method and basis set) and other less evident variables, such as

integral truncation criteria and grids. We can group these errors into two groups, which we will call discretization and modelization errors. Discretization errors cover those errors coming from the finite treatment of infinite series: basis set, sampling and truncation.⁷ Model errors refer to the method - the physical model used to describe a real system. Under this umbrella we have two quantum mechanical models: wavefunction and Density Functional Theory (DFT) methods. Whereas the former can build systematic improvements adding correlation on top of Hartree-Fock (HF), the latter are not prone to systematic improvement. However, wavefunction correlated methods are not generally available for solid state, so that basically all material science computations are done within the DFT framework. Within this framework, many exchange-correlation functionals are available. However, the increase in computational cost and theoretical involvement of the functional does not necessarily yield better results. This means that computational material scientists are left with the choice of functional and no security whatsoever of how the method is affecting the results (i.e. a more expensive functional will not necessarily lead to a better result). Having fixed all the remaining degrees of freedom of the simulation (which can be systematically improved), we will focus on the uncertainty related to working within the DFT framework, which is not predictable in advance, trying to answer the question: how is the model (functional) affecting the results? For this, one first needs to understand the main errors coming from solid state computations. These have been summarized as difficulties in modeling non-covalent interactions, strongly correlated systems and delocalized/fractional charges.⁸ In the absence of non-covalent interactions or strongly correlated systems (which are easy to identify), the main source error in DFT simulations is the ever-present delocalization error.⁹

Delocalization error

Delocalization error is the tendency of approximated methods to over-localize or over-delocalize electron density. The extreme behavior of over-delocalization is given by the Local Density Approximation (LDA). LDA describes the homogeneous electron gas. Hence,

it tends to delocalize electrons like in a metal. Semilocal improvements of DFT build on the Local Density Approximation, partially correcting for this feature, but still leading to over-delocalization. On the other extreme, Hartree-Fock (HF) is built to promote electron-pairing, yielding over-localized electrons. It is then easy to see that HF and LDA provide the upper and lower bounds to electron localization; this electron localization, in turn, affects physical and chemical properties. Let us see one prototypical example; conjugated double bond chains are especially prone to this error: whereas HF tends to localize electrons leading to stronger double bonds and weaker single bonds, LDA tends to make single and double bond distances similar to each other. These deviations can be summed up in one single number known as Bond Length Alternation (BLA):¹⁰

$$BLA = \frac{\sum_i l_{db,i} - l_{sb,i}}{i} \quad (1)$$

where $l_{db,i}$ and $l_{sb,i}$ are the lengths of adjacent double and single bonds. Large BLAs reveal that double and single bonds are very different in length and vice-versa. The effect of delocalization error can be easily grasped in Figure 2, where the evolution of BLA with the number of $-\text{CH}=\text{CH}-$ units is calculated with different methods. HF provides the least delocalized and LDA the most delocalized conjugated system. The reference value, CC2 (Second-Order Approximate Coupled-Cluster), as well as all other methods, fall within the HF/LDA range. The difference between the HF and LDA value, which already at two $-\text{CH}=\text{CH}-$ units represents 30% of the absolute value, is not constant, but increases with the length of the chain, leading to a dramatic difference between the two methods. In other words, this error is size-dependent, becoming crucial for big systems and solid state. Moreover, the lack of regularity of this error implies that a systematic scheme for correcting this problem is difficult to implement. However, knowing the limiting cases, we will see that an estimation of uncertainty can be designed for any crystal.

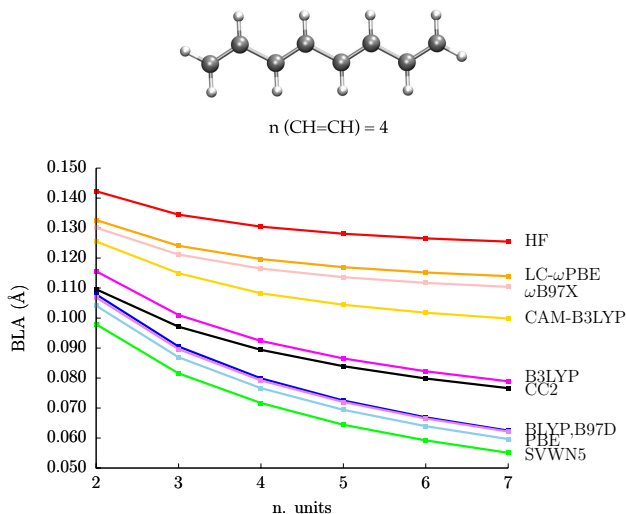


Figure 2: Bond Length Alternation (\AA) in a chain of conjugated double bonds as the length of the chain increases. Calculations carried out with different functionals, Hartree-Fock and CC2.

As a limiting example, we will consider the crystal structure of boric acid, belonging to space group $P3_2$, whose primitive cell is shown in Figure 3. $\text{B}(\text{OH})_3$ molecules are organized in sheets, parallel to the a, b plane and perpendicular to the c axis. The crystal is stabilized by a strong network of hydrogen bonds, while across-sheet contacts are regulated by electrostatic and dispersion interactions. Hence, we expect the results to be affected both by dispersion and delocalization error. Table 1 reports the experimental, HF and LDA values of: (i) intramolecular B–O bond distances (b_n), (ii) intermolecular $\text{O} \cdots \text{H}$ hydrogen bonds (hb_n), (iii) inter-sheet B \cdots O distance (BO) and (iv) lattice constants a , b and c .

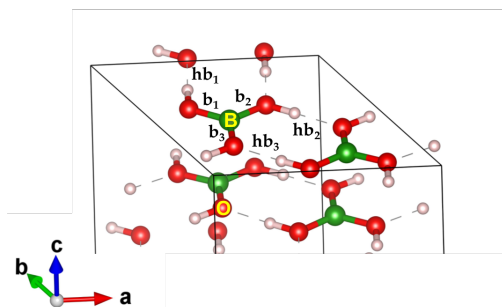


Figure 3: Structure of the $\text{B}(\text{OH})_3$ crystal. Main distances have been labelled as in Table 1.

Results clearly show that intramolecular distances are only slightly affected by the method

(b_1 to b_3). HF over-localization leads to shorter intramolecular bonds than LDA, but the overall accuracy is good and not subject to important deviations. However, both delocalization and dispersion errors add up in the same direction to give a wrong description of the non-bonded network. Too long intermolecular distances are obtained. The difference between the values is as large as 0.4 \AA for the hydrogen bonds (hb_1 to hb_3) and is even more dramatic when looking at the $B \cdots O$ distance (along c axis), which accounts for across sheet contacts: HF predicts a distance almost 1 \AA larger than LDA. This huge error in the non-bonded contacts leads to completely wrong cell parameters in the crystal. The result is reflected in cell parameters, where the difference between HF and LDA along c , where both dispersion and delocalization errors are present, is much larger than that along a and b .

Table 1: Geometrical parameters of the $B(OH)_3$ crystal: intermolecular distances and lattice constants. Bond labels refer to Figure 3. Distances are in \AA . The structure was resolved at $T=297 \text{ K}$. Basis set: TZVP for O and B and 3-1p1G for H.^{11,12}

Distances	HF	LDA	expt. ¹³
b_1	1.359	1.368	1.377
b_2	1.358	1.364	1.351
b_3	1.357	1.364	1.349
hb_1	1.874	1.398	1.822
hb_2	1.882	1.416	1.843
hb_3	1.880	1.411	1.911
B-O	3.697	2.758	3.187
a, b	7.244	6.628	7.045
c	11.080	8.412	9.561

This result is particularly significant because, as we will see, it persists when dispersion is included in the calculation and it also applies to a wide range of extended (covalent, ionic) systems, highlighting the relevance of the wrong energy description as a functional of the density and its consequences for computation.

Results and discussion

Ionic solids

With the aim of testing the hypothesis that HF and LDA can be used to assess the uncertainty of a calculation, we will start by discussing the properties of a set of ionic solids, where dispersion is expected to play a minor role. The HF and LDA values of cell parameter a are reported in Figure 4 (full set of structures and computational data available in ESI). They are invariably the upper and lower bound, respectively, for the experimental data, proving a robust computational error bar. The green and black bars represent the absolute and normalized amplitude, respectively, of the error bars associated to each structure. Let us have a look at the LiF-KI family of rocksalt structures. Whereas the absolute error bar in general increases with the size of the cell parameter, the normalized error bar remains fairly constant along the family (with the exception of the smallest structure, LiF). Similar considerations can be drawn for the other families reported in Figure 4, further suggesting that the delocalization error at the origin of the amplitude of the error bar is constant within a given family of structures. This is extremely interesting because it means that once that the effect of the delocalization error on one member of a given family is known, the corresponding uncertainty for different members of the same family can be quickly estimated (see ESI for an example). To the best of our knowledge, this is the first time that computational errors can be estimated from another compound. Moreover, such estimations are done on the basis of only one compound and can then be applied to other members of the family, meaning that quick *a priori* estimations can be done just based on the symmetry of the structure.

We also tested the HF-LDA bar on less common compounds, such as CuBr. For the III, V and VI phases, HF and LDA parameters have been compared with the accepted reference value, which is itself calculated (Tersoff potential).¹⁴ CuBr III and VI have a B3 and a B1 structure, respectively, and CuBr VI crystallizes in the SC16 tetragonally bonded structure. CuBr shows the highest error bar among the set of ionic compounds in Figure 4, more than

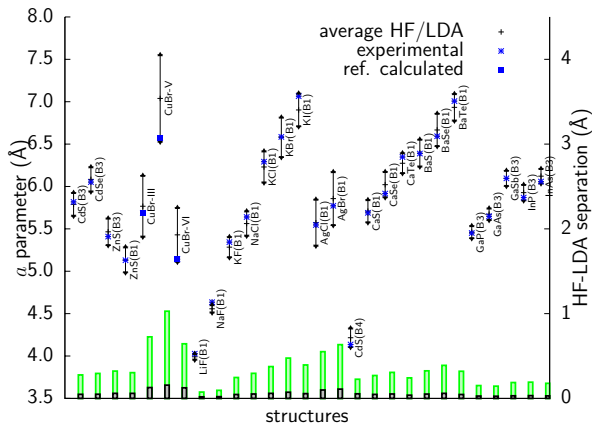


Figure 4: Calculated HF (top) and LDA (bottom) cell parameter a for 28 binary ionic solids with indication of the experimental reference value. Green bars represent the width of the error bar, black bars the same quantity normalized by the experimental cell parameter.

1 Å. This means that CuBr is extremely sensitive to the computational method, and a much more careful calibration is required than for studying a heavier binary compound like CaTe. Hence, this approach enables to identify those compounds whose computational simulation is more complicated (larger delocalization error) and whose choice of method should be dealt with care.

Molecular solids

The discussion of molecular solids is more complex due to several factors, among which thermal expansion and non-covalent interactions are particularly relevant. For small molecules, whose intermolecular distances contribute to the cell size (and thus the cell parameters) to a large extent, thermal expansion is significant and can involve volume expansion up to 8% moving from 0 K to room temperature.¹⁵ The standard calculation of cell parameters, which involves a minimization of the potential energy of the crystal, does not account for these thermal effects, that are included separately, usually by means of the Quasi-Harmonic Approximation (QHA). Additionally, DFT methods are plagued by an insufficient description of dispersion interactions, whose effect can be accounted for with a variety of methods.¹⁶ Dispersion interactions are attractive, and therefore shrink the cell. Overall, these two con-

tributions, thermal expansion and dispersion, go in opposite directions and partially cancel out (see ESI for a full discussion). This is evident when looking at Figure 5, which shows the experimental values and HF-LDA error bars calculated for a series of molecular solids without accounting for thermal or dispersion effects. In spite of the other model errors (dispersion), all experimental values of cell parameters fall within the error bars, with the only exception of acetylene crystals. For acetylene crystals, both cubic and orthorhombic, the failure of the HF/LDA error bar can be attributed to an important discretization error related to the basis set, as discussed in the ESI.

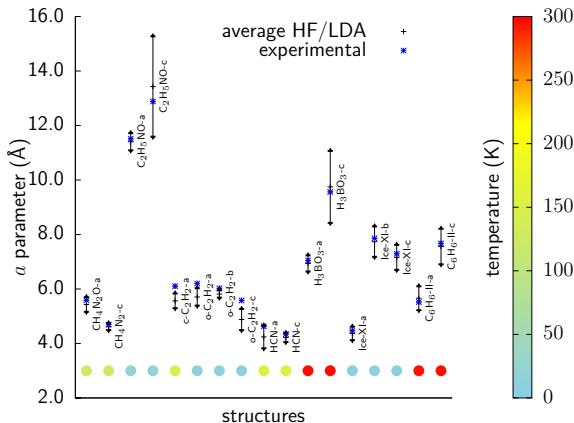


Figure 5: Calculated HF (triangle) and LDA (inverted triangle) cell parameters for 8 molecular solids with indication of the experimental reference value. The temperature corresponding to the experimental observation is reported.

The width of the error bar is much larger for molecular solids than for ionic ones (Figure 5). As already discussed for Table 1, this is due to the dependence of intermolecular distances on the method employed. As mentioned, dispersion and thermal effects have opposite effects on lattice constants and therefore partially cancel out. An extensive analysis of these two effects and their interplay is reported in the ESI and shows that their combined effect on cell parameters is significantly inferior to the HF/LDA separation. This implies that our simple HF/LDA model, which uses the potential energy and does not account for thermal or dispersion effects, can also be applied to molecular solids for assessing the sensitivity of the system to delocalization error.

Transition pressures

We have shown that the uncertainty associated to DFT calculated cell parameters can be expressed in terms of the HF and LDA values, and that this error is some orders of magnitude higher than the corresponding experimental uncertainty. In this sense, the case of cell parameters is: *(i)* a proof-of-concept of the validity of our model, *(ii)* an inductive proof of how this difference can be used to estimate how much a given computation depends on the model (functional) chosen. However, it is not useful in the experiment-theory validation due to the extremely low experimental uncertainty.

The mutual validation of measured and simulated quantities along with their error bars can be recovered when tackling experimentally less accessible quantities, such as transition pressures. Transition pressures are commonly used to assess the quality of DFT functionals,¹⁷ and they can have an associated experimental uncertainty up to 2.9 GPa even for simple structures.¹⁸ This uncertainty derives from a complex set of factors, including the accuracy of the pressure and temperature readings of the sample during the crystallographic measurement.¹⁹

What happens when we look at HF and LDA derived transition pressures? Similarly to what was reported for cell parameters, LDA and HF bracket the experimental values. Which one overestimates and which one underestimates the correct value depends on the relative nature of the phases involved. In the cases that we tested, essentially B1 to B2 transitions of alkali halides, HF overestimates and LDA underestimates transition pressures; this is due to the fact that the B2 phase of alkali halides is more compact and thus more favored by LDA than the B1 phase. If the situation was opposite, i.e. a structure with a more localized bonding picture in the second phase, then we would expect the opposite behavior, with LDA the upper and HF the lower bound of the bar. In both cases, we expect functionals to fall within the HF/LDA bar. Figure 6 shows the HF and LDA values of a series of transition pressures. For the B1 to B2 transition of alkali halides, we see that again the experimental value falls between the HF and LDA values.¹⁸ This holds even for large systems (KCl to KI),

which are characterized by very low transition pressures. In these cases, LDA inverts the order of stability of the two phases, which has been plotted as a transition pressure of zero. In these cases, the error bar becomes crucial to determine the transition sequence. Just like for the cell parameter, it is easy to see that the choice of functional should be handled with much more care for ZnS (B3 to B1 transition) than for alkali halides.²⁰ But what is more interesting, in all cases, our computational uncertainty is of the same order of magnitude as the experimental one. Hence, the delocalization error based computational uncertainty can be directly compared with the experimental error bar to mutually assess the quality of the results.

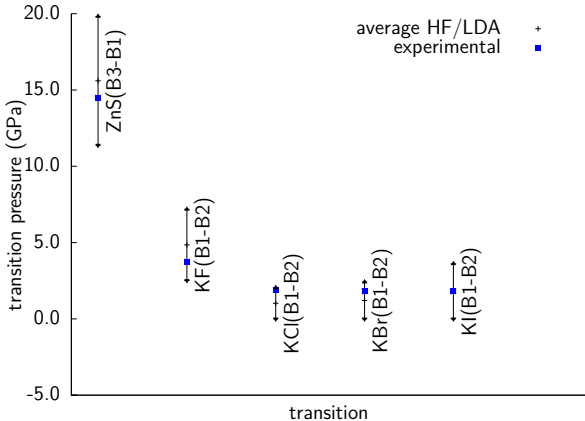


Figure 6: Calculated HF (top) and LDA (bottom) transition pressures (GPa) with indication of the reference experimental value.

Conclusions

Summarizing, we carefully constructed an extensive database of experimental data (cell parameters and transition pressures) at low temperature that is available in ESI and should be of large use in the comparison of experimental and theoretical data. We used these data to show that the choice of DFT functional for the simulation of solid systems greatly affects both cell parameters and transition pressures. This is attributed to the well-known delocalization error of DFT, and it has been shown that HF and LDA provide a robust error

bar for the calculated values. After validating our model on cell parameters, we focused on transition pressures, and showed that for experimentally less precise data, HF and LDA can yield an error bar of the same order of magnitude as the experimental one.

The general picture that emerges from this study is that a paradigm shift in the interaction between experimental and computational chemistry is needed. The different nature of the errors involved requires a different approach for error estimation. Experimental measures require several repetitions to assess their reproducibility. Since simulation errors are systematic, the estimation of the error must go through the repetition under different conditions and the search of limiting behaviors.

Too often simulation parameters are tuned case by case, according to the so-called calibration,²¹ to match as closely as possible a given available experimental value, when there is no guarantee that the agreement is not the result of error cancellation, and, consequently, that this same agreement will be preserved for a property outside the calibration set. Rather, we propose a property-specific approach that provides an a priori assessment of the method dependence with two calculations for each property. The idea is to compute the overall HF/LDA separation for the given property and compare it with the separation between the experimental value and the functional that one wants to test.

The advantage of this approach over a plain comparison of DFT and experimental values is that we are no longer looking at the absolute DFT-experimental difference, which will largely depend on the property under scrutiny (e.g. small for cell parameters and large for transition pressures), but rather at the ratio between it and the maximum method-dependent error corresponding to the HF/LDA bar. When the basis set and all other simulation parameters except the method are kept fixed, we can attribute the difference in the results to the method only. Thus, in practice, if the DFT-experimental difference is much smaller than the HF/LDA bar, it means that the method provides, among the many possible functionals, a good description of the property under study; on the other hand, the DFT-experimental separation is almost as large as the HF/LDA bar, it means that we are making a significant

error, and the corresponding functional should be discarded. A limitation of this approach is that it involves performing a HF calculation, which is quite expensive when using plane wave basis sets. However, when using a plane wave code hybrid functionals are not accessible for complex systems for the same reason, i.e. the cost of calculating the exchange integrals, and thus the choice of DFT functionals is intrinsically limited.

Overall we have devised a simple and robust indicator to guide the computational chemist in the choice of the simulation setup for materials science.

Supporting Information Available

List of HF, LDA, PBE and experimental cell parameters; comparison between HF, LDA and PBE; list of HF, LDA and experimental transition pressures; discussion of the computational parameters employed; analysis of the effect of changing the implementation of the LDA functional; discussion of the effect of dispersion interactions in molecular solids; discussion of the effect of thermal expansion in molecular solids; analysis of a particular case: cubic acetylene; discussion of the prediction capability of the HF/LDA bar; discussion on the effect of the fraction of exact exchange. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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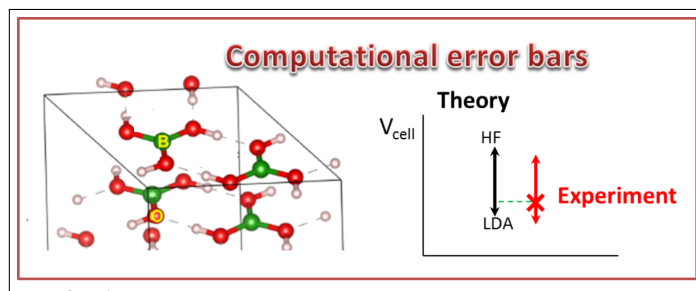
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